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THE EFFECT OF MICROORGANISMS ON THE PROPERTIES OF PORCELAIN MIXTURES IN MATURING (A Review)

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The reasons for the modification of the structure and properties of porcelain mixtures subjected to maturing are analyzed in the context of laws governing of the evolution of microbial communities. It is shown that introduction of a nutrient substrate to a porcelain mixture stimulates the activity of natural microflora which is accompanied by favorable modification of the coagulation and condensation structure. The sintering process is concurrently intensified and the degree of "ripening" of porcelain is increased.

Maturing of ceramic materials has been known since the Bronze Age [1]. Maturing as a method for improving plasticity is used mostly in the production of porcelain articles. The method consist in long-term storage of a prepared porcelain mixture in a dark, warm, and humid place, usually in the form of relatively small lumps of material stored in a basement. The increase in plasticity is attributed to bacterial processes and increasing content of colloid particles in clays [2]. As this takes place, organic compounds in the mixture putrefy, soluble compounds are washed out, sulfuric compounds are oxidized, etc. Long-term maturing of a porcelain mixture in a humid state is accompanied by a substantial increase in its plasticity, which makes it possible to mold mixtures which contain a substantial share of non-plastic components and provides for high whiteness and translucence of porcelain. As a rule, small quantities of mixtures are allowed to mature for 25 – 100 years.

There are different opinions regarding the necessity of maturing materials. On the one hand, some authors believe that maturing of material at a contemporary ceramic factory is not advisable, since it involves additional capital costs of constructing and maintaining premises for mixture storage. On the other hand, it is established that as a consequence of maturing, heterogeneity of mixtures is decreased, their plasticity increases, drying sensitivity becomes lower, and mechanical strength is increased. It should be taken into account as well that processing plastic ceramic mixtures by standard contemporary machines does not impart those high technological qualities that used to be attained in long-term maturing. For example, an unsatisfactory design of vacuum-press nozzles causes anisotropic texture (orientation of particles) in plastic mixtures, which persists in molded articles as well [3]. Anisotropic texture of a porcelain mixture causes internal stresses which in drying and firing result in deformation of porcelain.

The microflora of matured porcelain mixtures and their components has not been previously studied; neither are the processes taking place in mixtures in long-time maturing investigated. However, certain known data point to a possibility of significantly decreasing the duration of ceramic mixture maturing due to the effect of microorganisms. The effect of microorganisms consists in improving properties of ceramic mixtures in the plastic state, as well as favorable modification of the structure and properties of porcelain [4 – 6].

The impact of microorganisms on mineral materials was studied in researching the biological erosion processes in the hypergenesis zone and in attempts to develop microbiological processes for extracting valuable components from mineral materials. The obtained results were analyzed in detail in several reviews published in Russia and abroad [7, 8]. It was shown that a wide range of microorganisms (microfungi, autotrophic and heterotrophic bacteria, microalgae) affect aluminosilicate minerals and facilitate dissolution of elements which are part of their crystal structures.

Heterotrophic microorganisms which evolve in media with organic compounds affect various types of minerals. Heterotrophic bacteria and microfungi extract elements from kaolinite, muscovite, etc. [9, 10]. Entrainment of elements into a solution under the effect of microorganisms was also

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observed in studying their effect on different minerals: granites, sandstones etc. [8].

One of the developing trends in using microorganisms for silicate destruction, concentration of mineral materials, and improvement of porcelain mixture properties involves a group known as "silicate" bacteria. Strains of the species *Bacillus mucilaginous subsp. siliceus* were isolated and described by V. G. Aleksandrov and his colleagues [11]. The authors believed that "silicate" bacteria are capable of consuming energy released in destruction of the crystal lattice of silicates and do not need organic matter for their growth.

The insufficient substantiation of V. G. Aleksandrov's concept of the existence of "silicate" bacteria was first commented by K. I. Surman [12] who obtained experimental proofs of the fact that *B. mucilaginosus* is a normal heterotrophic soil bacillus which needs organic compounds for its growth.

These data were later confirmed in a more detailed study of different strains of *B. mucilaginosus* [13, 14]. It was also demonstrated using labeled carbon dioxide ($^{14}CO_2$) that *B. mucilaginosus* is incapable of autotrophic growth and fixation of CO_2 both in the presence and in the absence of silicate minerals [15].

According to the contemporary notions [7, 8], the mechanism of the impact of microorganisms on silicate minerals is based on indirect processes: minerals are affected by various products of microbic metabolism, i.e., mineral and organic acids, biogenic alkalis, exopolymers, in particular, exopolisaccharides. The process of destruction of minerals in the general form is described by the equation

$$M^+ \text{ mineral}^- + H^+OH^- \rightarrow H^+ \text{ mineral}^- + M^+OH^-,$$

where M^+ mineral$^-$ is the initial mineral and H^+ mineral$^-$ is the eroded mineral; M^+ are metal cations contained in the mineral.

All processes affecting the concentration and the state of reactant compounds and reaction products have an effect on the rate of the erosion processes.

Sulfuric and nitric acids produced by autotrophic microorganisms affect silicates, since they are sources of H^+ ions.

Heterotrophic microorganisms which produce organic acids enrich the medium with H^+ ions, as well as with organic ligands and complex-formers, including all di-, tri-, and polycarbonic acids and oxy- and keto-acids. Such acids bind metal cations in stable complexes and thus facilitate their extraction from minerals. Bacterial exopolysaccharides facilitate the destruction of silicate minerals by forming organosilicon compounds.

Along with research on microbiological processes taking place in erosion of mineral rocks and in soil formation, and studies of the possibility of microbial concentration of ore materials, certain studies were performed to determine the possibility of using microorganisms in the ceramic industry. Russian scientists used only strains of what is known as "silicate" bacteria out of the whole variety of microorganisms. A multiple introduction of *B. mucilaginosus* cell suspension directly into the clay suspension with periodic washing by water makes it possible after 50 days of treatment to increase the specific surface and plasticity of the ceramic mixtures, as well as the mechanical strength of fired materials (USSR Inventor's Certif.658112b). A. S. Vlasov and colleagues [4 – 6] established the positive effect of introducing *B. mucilaginosus* strains on the rheological properties of ceramic materials and porcelain mixtures, as well as the quality of ceramic tiles.

Various bacteria and microfungi were used to improve the moldability and granulometric composition of clays and kaolins, adding hydrocarbons as a nutrient medium [16].

A method for improvement of clays directly in quarries was suggested as well. For this purpose, wastes from microbiological production enriched with organic materials were introduced into mineral rocks, which stimulated the growth of microflora in clays.

In France, an attempt was made to introduce additives of glucose and microbial polysaccharide (xanthane) to a clay suspension in the course of its preparation [17].

Chemical methods based on leaching iron with mineral and organic acids provide for a high degree of refinement of the initial components [18]. However, these methods are costly, technologically hard to implement, and environmentally unsafe.

Microorganisms in natural conditions take part both in oxidation of bivalent iron and in reduction of trivalent iron [19]. Dissolution of iron-bearing compounds proceeds under the effect of organic acids and certain microbial metabolites which are complex-forming agents [19], or as a consequence of enzymatic and nonenzymatic reduction of iron.

At present, the following main groups of microorganisms reducing iron are distinguished [20]: microorganisms using Fe(III) as electron acceptor (bacteria performing dissimilative reduction of iron, certain strains of sulfate-reducing bacteria, certain thiobacilli, heterotrophic bacteria, and fungi) and microorganisms indirectly causing reduction of iron by the products of their metabolism (sulfate-reducing bacteria, enzymatic microorganisms, aerobic heterotrophic bacteria).

If an organic agent is introduced in a porcelain mixture subjected to maturing, this can initiate processes in the mixture similar to gley processes in soils. Gley processes usually proceed in anaerobic conditions with participation of complex compositions of microorganism communities and obligatory presence of organic material, in conditions of increased humidity. Gley formation is accompanied by conversion of oxides to lower oxides and unbalanced entrainment of iron. An essential visual indicator of the gley process is the grayish-blue color of the clay-bearing material. This typical color is attributed to the reduction of trivalent iron [9].

Thus, application of known methods and development of new techniques of microbiological treatment of mineral material using the mechanisms of functioning of microbial com-

munities is a promising and probable way for solving the problem of deferrization of ceramic mixtures.

Knowledge of the specifics of vital activity of the main groups of microbes and the composition of dominant microorganisms in the maturing of ceramic materials and porcelain mixtures will make it possible to control the deferrization process by using corresponding nutrient substrates and controlling the composition of the microorganism community.

The purpose of the present work is to study the dynamics of evolution of microorganisms in a porcelain mixture during maturing and the effect of microbiological processes on the properties of porcelain mixtures. The variants of experiments are shown in Table 1.

The porcelain mixture had the following composition (wt.%): 41 Prosyanovskii kaolin KF-3, 6 Chasov-Yarskii clay "ChO", 20 Glukhovetskii quarz sand PK-93, 29 Chupinskii crushed pegmatite KPShM-02-2, 2 scrap (industrial) of products after the first firing, and 2 scrap (industrial) of products after the second firing.

A suspension for the experiments in storing porcelain mixture was prepared by the separate-joint method. The grog components were crushed in a ball mill holding 30 liters, the ratio of grog materials : milling bodies : water being equal to 1 : 1 : 1, to a prescribed level of dispersion, after which the plastic components were added. Dispersion of the experimental mixtures was characterized by a residue 1.0 – 1.2% on a sieve No. 0056. The suspension was poured through a No. 01 sieve, subjected to magnetic separation; next, the additives were introduced in it according to the design of the experiment (Table 1), the suspension was held for 1 day, then the rheological properties of the porcelain suspension were measured, and the suspension was dehydrated in gypsum molds to 25% moisture. The obtained filter cakes of the porcelain mixture were stored for 90 days at the temperature of 28°C.

During maturing of the porcelain mixture, its samples were periodically taken to determine color indexes, the reflection coefficient in the visible spectrum range, and to analyze the microflora composition.

TABLE 1

Basic parameters	Mixture index*			
	ZhO	VK	VB	VS
Moisture, %, %	25.0	25.0	25.0	25.0
Storage temperature, °C	–	28	28	28
Synthetic medium with glucose, ml/kg	–	–	–	250.0
Liquid culture of *B. mucilaginosus*, ml/kg	–	–	250.0	–
Maturing duration, days	–	90	90	90

* ZhO) fresh reference mixture without additives and not subjected to maturing; VK) reference mixture without additives subjected to maturing; VB) porcelain mixture with addition of *B. mucilaginosus* liquid culture VKMB 1480D grown on a synthetic medium with glucose; VS) porcelain mixture in which growth of natural microflora was stimulated by adding a nutrient medium.

The quantitative account of aerobic and anaerobic microorganisms in porcelain mixtures in the course of maturing was performed using the limiting culture method in traditional microbiological media [21]: diluted (1 : 10) meat infusion broth for aerobic heterotrophic microorganisms, Vinogradski medium for anaerobic fermenting microorganisms, Postgate medium with sodium lactate (4 g/liter) for sulfate-reducing bacteria, and Giltay medium without asparagine for denitrifying bacteria.

The porcelain whiteness was assessed according to the requirements of GOST 24768–81. The spectral reflection coefficients and the color coordinates of the mixture and the porcelain in the LAB system (MKO-76) were measured by a Pulsar spectrocolorimeter [22].

The plastic strength of the porcelain mixtures was determined on a conic Rebinder plastometer. The optimum molding moisture was determined graphically from the dependence of plastic strength of the mixtures on their moisture. The samples (diameter 12 mm, length 100 mm) were fired in a flame furnace. The water absorption of the fired samples was determined by GOST 25092–82, the static bending strength was determined in accordance with GOST 19286–77, and the dynamic bending strength was measured on a pendulum testing machine of the type PSV-0.4.

The parameters of the threshold and intensity of structure formation were determined in accordance with GOST 19609.16–88. The values of the threshold and the intensity of structure formation were determined graphically. The filtration capacity was determined in accordance with GOST 19609.24–88 on a VM-6 instrument.

The parameters of the porcelain suspension characterizing its structural properties are shown in Table 2.

It follows from Table 2 that as a consequence of introducing *B. mucilaginosus* liquid culture grown on a synthetic medium with glucose into the porcelain suspension VB, the properties of the latter are significantly modified: its filterability decreases (from 4.9 to 2.1 $cm^3/min^{0.5}$), and its threshold and intensity of structure formation increase. According to data in [23], such simultaneous modification of three parameters point to a decreased level of aggregation and increased dispersion of clay particles in the porcelain suspension, as the peptization (disaggregation) process prevails. The destruction of clay particle aggregates caused by the presence of the bacterial culture *B. mucilaginosus* in the porcelain suspension VB can be attributed to the effect of

TABLE 2

Parameter	Mixture index		
	ZhO	VB	VS
Suspension moisture, %	51.61	53.75	52.09
Suspension density, 10^3 kg/m^3	1.43	1.40	1.42
Filterability, $cm^3/min^{0.5}$	4.87	2.12	4.53
Structure formation threshold, 10^3 kg/m^3	1.115	1.165	1.100
Intensity of structure formation, 10^3 $(kg/m^3)^{-5}$	1.80	2.90	1.70

B. mucilaginosus exopolysaccharides which are metabolites of these bacteria and possess surfactant properties.

Thus, introduction of *B. mucilaginosus* liquid culture into the porcelain mixture VB results in a modification of its coagulation-thixotropic structure as opposed to the similar structure of the reference mixture ZhO and the experimental mixture VS, even before the filtration cakes are stored for maturing.

The dynamics of the evolution of microorganisms in porcelain mixtures in storage is shown in Table 3.

The quantitative account of microorganisms indicated that aerobic heterotrophic microorganisms represented mostly by bacteria whose number reaches 10^6 cells/g of mixture are present in the reference samples and in the experimental samples with additives of nutrient medium and *B. mucilaginosus* liquid culture. The quantity of anaerobic microorganisms does not exceed 10 – 100 cells/g. This is natural microflora which penetrates into the porcelain mixture simultaneously with the initial components.

In the course of maturing of the reference mixture VK, no variations were registered with respect to the quantity and composition of the main tested groups of microorganisms. The cake color did not vary either. Apparently, the proper components of the porcelain mixture do not contain substrates in sufficient concentrations to ensure the activity of the microflora.

Addition of a nutrient medium (variant VS) or *B. mucilaginosus* liquid culture (variant VB) to the mixture contributed to quantitative growth of microorganisms and was accompanied by sharp differentiation of the microflora of the inner and outer layers of the cake. Aerobic and facultatively aerobic bacteria prevailed in the cake outer layers, and their number by the end of the first month of storage increased up to $10^8 – 10^9$ cells/g of mixture. The amount of yeast and microscopic fungi on the cake surface also increased by the end of the experiment, whereas none of these microorganisms were isolated from the internal layer. The quantity of aerobic microorganisms in the internal layer decreased to $10^3 – 10^4$ cells/g, and by the end of the experiment, to 10 – 100 cells/g of mixture, but the number of sulfate-reducing and fermentative bacteria increased, and their quantity amounted to 10^4 and 10^6 cells/g, respectively, after one month of storage, and 10^8 and 10^6 cells/g by the end of the experiment (Table 3).

Introduction of *B. mucilaginosus* liquid culture into the porcelain mixture VB stimulated the growth of microflora in the porcelain mixture, since the medium in which the strain *B. mucilaginosus* 1480D was cultivated was identical to the nutrient medium introduced into the porcelain mixture VS.

The amount of *B. mucilaginosus* culture did not vary in storage of the porcelain mixture and amounted to $10^4 – 10^5$ cells/g both in the inner and outer layers of the cake.

Thus, the quantitative account of microorganisms reveals that the porcelain mixture contains various groups of microorganisms, whose growth and activity become possible only on adding a nutrient substrate to the porcelain mixture. In the presence of the substrate, the microflora develops and is differentiated in the inner and outer layers of the cake. In accordance with the different compositions of microflora in the outer and interior layers of the cake, they become differentiated in color. The predominant development of anaerobic microflora in the internal layers of cakes is accompanied by changes in the color of mixture, which propagate from the center to the periphery of the cake, as maturing duration is extended. The bluish-green color of the mixture was typical of the zones with developing anaerobic microflora. By the end of the experiment, the thickness of the light yellow outer layer did not exceed 2 – 5 mm.

Since the mineral base of the porcelain mixture is represented by non-tinted components, i.e., feldspar, kaolinite, and quartz, the main chromophores are iron and titanium compounds. The forms of ferric compounds and their identification in the porcelain mixture composition are given in [24]. As ferric compounds in the porcelain mixture transform under maturing, the mixture changes its color. The spectrophotometric and colorimetric methods were used to identify these transformations. These methods are based on the fact that the color of mixture samples depends on the system of color centers which have different spectral absorption zones depending on their type [25].

Figure 1 presents the reflection coefficients in the visible spectrum range for the internal layers of the reference and experimental porcelain mixture cakes. The reflection spec-

TABLE 3

Mixture index	Cake layer	Microorganisms, cells per 1 g of porcelain mixture								
		aerobic heterotrophic bacteria			sulfate-reducing bacteria			fermenting bacteria		
		0 days	30 days	90 days	0 days	30 days	90 days	0 days	30 days	90 days
ZhO	–	10^6	–	–	10^1	–	–	10^1	–	–
VK	Outer	10^6	10^6	10^5	10^1	10^1	10^1	10^2	10^1	10^1
	Internal	10^6	10^5	10^5	10^1	10^1	10^1	10^1	10^1	10^2
VB	Outer	10^6	10^8	10^6	10^1	10^1	10^2	10^1	10^2	10^1
	Internal	10^7	10^4	10^2	10^1	10^4	10^6	10^1	10^6	10^6
VS	Outer	10^6	10^9	10^8	10^1	10^1	10^2	10^1	10^2	10^2
	Internal	10^6	10^4	10^2	10^1	10^4	10^8	10^1	10^6	10^6

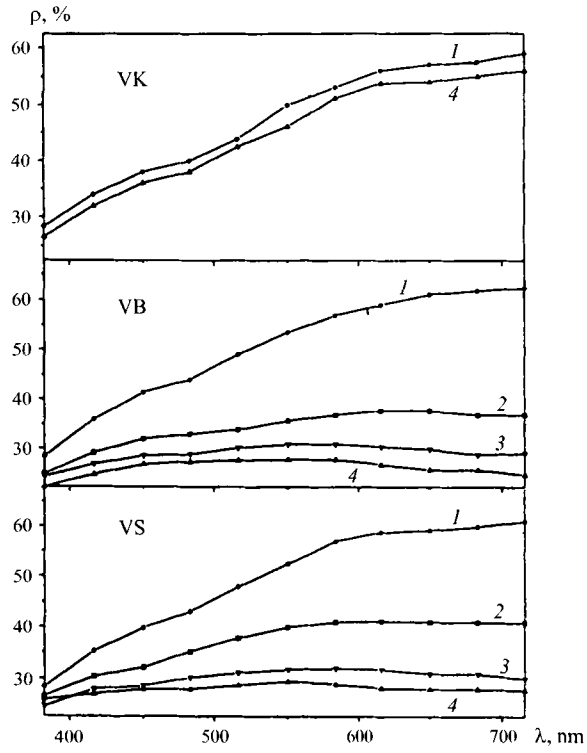

Fig. 1. Variation in reflection spectra of porcelain mixtures in storage: *1*) initial; *2*, *3*, and *4*) after 30, 60 and 90 days of maturing, respectively.

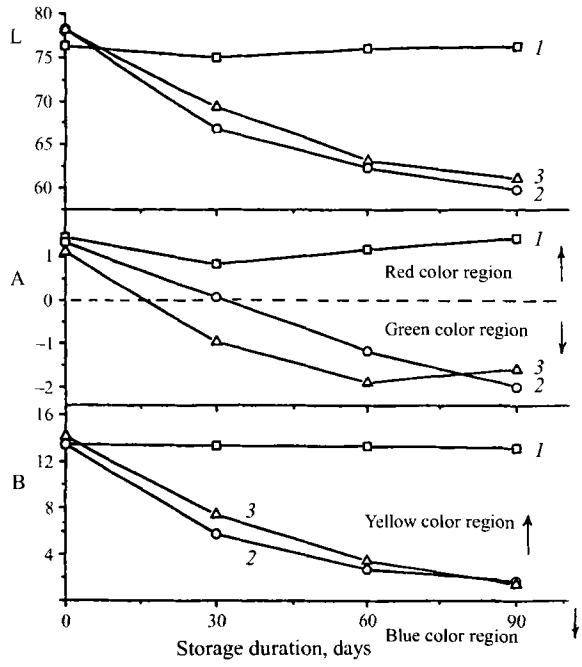

Fig. 2. Variation of the color of porcelain mixtures in storage in the coordinates of equal-contrast colorimetric system LAB (MKO-76): *1*, *2*, and *3* are mixtures VK, VB, and VS, respectively.

trum curves of the outer layers are not shown, since they did not vary in the course of the experiment.

As can be seen, the shape of the spectrophotometric curve of the internal layers of VK samples virtually does not change. The shape of the initial spectrophotometric curves of samples VK, VB, VS points to the predominant presence of Fe(III) ferric compounds in the mixture, which have the absorption maximum in the ultraviolet and short-wave ranges of the visible spectrum. The variation of the shape of the reflection curves (curves *2*, *3*, and *4*) of experimental mixtures VB and VS in the course of maturing points to transformation of ferric compounds under the effect of microorganisms. The low reflection coefficients in the entire visible spectrum range of experimental mixtures VB and VS (curve *4*) testify to the synthesis of ferric compounds which absorb light energy.

The former compounds include newly synthesized ferric compounds of the type of magnetite and pyrite. These iron compounds were identified in clay-bearing materials treated by a microbic community [26 – 28]. The microbiological origin of the magnetite formed is supported by the fact that no increment of magnetite is observed in the reference kaolin sample, and by the presence of representatives of different groups of iron-reducing bacteria in the composition of the microbic community [29]. Moreover, due to the destruction of newly synthesized iron-organic complexes by bacteria consuming their organic components, iron can be reprecipitated in the form of insoluble compounds, such as ferric hydroxides, sulfides, and phosphates. The liquid above the sediment exhibited suspended black-colored particles either in the form of amorphous compounds, or in the form of weakly crystallized colloid particles of pyrite and vivianite [28].

Figure 2 presents the chromaticity coordinates of the reference and experimental porcelain mixtures in different periods of maturing. As can be seen, the color coordinates of all porcelain mixtures before maturing were positioned in the red-yellow region. This is indicated by the positive values along the red-green (A) and the yellow-blue (B) chromaticity coordinate axes in the LAB system (MKO-76). This color of porcelain mixtures indicates the presence of iron oxides and hydroxides of the type of hematite, goethite, and hydrogeothite which have bright red or yellow-brown color.

It can be noted that the values of the luminosity index of the internal layer of experimental mixtures VB and VS in the course of maturing decrease in direct proportion to a decrease in the color saturation, and the color tone values were shifted from the red-yellow to the green-blue region of the chromaticity coordinates. It is evident that the main contribution to the decrease in the internal layer luminosity is made by the losses due to selective absorption of light by the color centers. The identical processes of modification of chromaticity coordinates in the internal layers of the experimental mixtures VB and VS through the entire maturing period attest that the processes of transformation of iron compounds in these mixtures are identical. Thus, the decrease in the luminosity of the internal layers of a porcelain mixture until a gray color is attained is due to the synthesis of magnetite and

pyrite compounds, and the green-blue tint is due to the formation of Fe(II) compounds.

The results of analysis of the rheological properties of the plastic mixtures after maturing revealed the following specifics: the mixtures VS and VB had a lower value of the optimum molding moisture and a narrower plastic state interval, whose narrowness is caused by the decreased moisture and yield point, whereas the value of the rolling point moisture remains stable.

Thus, in the course of maturing, the coagulation structure of the porcelain mixtures VB and VS, to which the nutrient medium intensifying the life of bacteria was added, changes more significantly than the corresponding structure of the reference mixture VK subjected to similar maturing conditions. Such modification of the rheological properties of the porcelain mixtures VB and VS is possible due to the destruction of aggregates and dispersion of clay particles, which contributes to an increased quantity and modified type of coagulation contacts of the disperse phase particles.

It is known that the coagulation structure acts as a matrix, and the subsequent structures, including the condensation and, later, the crystallization structures are formed on the basis of this matrix [29]. While a porcelain mixture with addition of a liquid bacterial culture or a nutrient medium stimulating the activity of natural microflora is maturing, microaggregates of clay particles disintegrate as the result of anaerobiosis, and the contacts between the silicate mineral particles are disturbed; the morphology of the kaolin particle surface is modified due to disintegration of a part of the crystals and their surface amorphization, while preserving the structure of kaolinite; the mineral and disperse compositions are modified as well, in particular, free iron compounds: easily soluble compounds are formed, the fraction of amorphous and weakly crystallized iron compounds increases, and muscovite is partly destroyed. In the course of drying of the porcelain mixture, coagulation contacts are transformed into condensation contacts, compounds are transferred via the vapor phase and deposited on the disperse phase particles, mostly clay particles, up to the emergence of condensation-crystallization contacts with the intermediate finely disperse phase, i.e., a solid solution which, primarily, more strongly binds single particles using the phase contacts (bridges) and, secondly, is in a more active state with respect to subsequent recrystallization, i.e., centers of activation of the process are formed.

As can be seen in Table 4, experimental samples of porcelain mixtures VB and VS after drying at temperature 1100°C exhibit high values of apparent density and bending strength. It is interesting to note a certain increase in the bending strength of the reference sample made of mixture VK subjected to the same maturing conditions, as opposed to the reference sample ZhO not subjected to maturing.

Mixture samples were fired in standard flame kilns according to the regime accepted for firing household porcelain (Table 5).

Sintering of porcelain samples made of experimental mixtures VB and VS and the reference mixture VK proceeds with higher intensity than that of the sample ZhO not subjected to maturing. Apparently, the interval of the sintered state for VS and VB is shifted to a lower temperature region and expands by 20°C in firing (1300 – 1380°C versus 1320 – 1380°C).

Table 6 shows the physicomechanical properties of experimental and reference porcelain samples fired in a flame kiln at the maximum temperature of 1320 for 22 h in a weakly reducing medium.

It follows from the data in Table 6 that, first, static bending strength increases only in the samples of VB and VS

TABLE 4

Parameter	Mixture index			
	VK	VB	VS	ZhO
Apparent density, 10^3 kg/m^3	1.67	1.68	1.68	1.67
Bending strength, MPa, after drying at temperature 110°C	2.13	2.43	2.66	2.00

TABLE 5

Parameter	Mixture index			
	ZhO	VK	VS	VB
Apparent density, kg/m^3, at firing temperature, °C				
1200	2.24	2.22	2.23	2.25
1250	2.41	2.37	2.38	2.37
1280	2.43	2.44	2.42	2.42
1300	2.45	2.46	2.49	2.46
1320	2.46	2.48	2.50	2.47
1350	2.45	2.46	2.47	2.44
1380	2.42	2.43	2.42	2.42
Open porosity, %, at firing temperature, °C				
1200	9.34	10.74	8.28	8.71
1250	4.07	2.77	2.79	2.06
1280	1.64	0.98	0.53	0.30
1300	0.60	0.20	0.00	0.01
1320	0.00	0.00	0.00	0.00
1350	0.00	0.00	0.00	0.00
1380	0.00	0.00	0.00	0.00

TABLE 6

Parameter	Mixture index			
	ZhO	VK	VB	VS
Strength:				
impact strength, kJ/m^2	2.08	2.21	2.21	2.20
bending strength, MPa	90.73	90.80	97.81	96.28
Density, 10^3 kg/m^3:				
apparent	2.40	2.41	2.48	2.45
true	2.50	2.50	2.54	2.53

mixtures which also exhibit high values of true and apparent density; second, the impact strength increases in samples of VB, VS and VK mixtures subjected to maturing which are also characterized by a higher degree of "ripening" of porcelain [30]. With respect to the degree of homogenization of the heterophase porcelain matrix J_h, samples are arranged in the following order: J_h(VB, VC) > J_h(VK) > J_h(ZhO) and, respectively, 1.67 > 1.61. > 1.52 (Table 7). The dissolution of quartz in firing proceeds more actively in the porcelain made of mixtures with bacterial culture and nutrient medium additives: J_q(VS, VB) > J_q(VK) > J_q(ZhO).

It is known [3] that the value of bending strength of porcelain is primarily related to its microporosity: the shape, size, relative arrangement, and the statistical function of pore distribution over the volume; the impact strength value is related to the degree of "reinforcement" of the structure by newly formed crystals, mostly, needles of primary mullite and prisms of secondary mullite. At the same time, it is obvious that the increase in the impact strength combined with the increased luminosity of porcelain samples (Table 8) arise from the shift in the ratio of the primary (scaly) mullite and the secondary (needle-shaped) mullite toward an increased content of secondary mullite.

Thus, maturing of porcelain mixtures intensifies the process of structure formation in porcelain; however, this process is more active in mixtures in which additives stimulate growth and activity of microorganisms.

The color characteristics of porcelain are given in Table 8. It should be noted from the beginning that microbiological treatment of porcelain mixtures was performed without subsequent treatment by washing, magnetic separation, etc. The chemical composition of experimental porcelain samples is virtually identical to the composition of reference samples.

TABLE 7

Mixture index	Phase composition, %			Degree of ripening	Quartz dissolution
	Crystalline phase		Vitreous phase		
	mullite	quartz			
ZhO	29	19	52	1.52	0.41
VK	29	18	53	1.61	0.45
VB	25	15	60	1.67	0.54
VS	25	15	60	1.67	0.54

TABLE 8

Sample index	Whiteness, %	Chromaticity coordinates				
		L	A	B	S	T
ZhO	54.0	82.0	– 1.24	5.83	6.0	102.0
VK	56.4	84.0	– 1.00	5.30	5.4	100.6
VB	59.5	84.6	– 1.55	5.51	5.7	105.8
VS	59.0	84.7	– 1.44	5.49	5.6	104.7

It follows from the data in Table 8 that the luminosity of samples VK, VB, and VS made of mixtures subjected to maturing is higher than the luminosity of samples of the reference mixture ZhO. The color saturation of samples of the former mixtures decreased insignificantly from S = 6.0 to S = 5.4 – 5.6, but the color tone and, accordingly, the chromaticity coordinates vary in different ways, depending on the composition: sample of mixtures VB and VS containing additives ensuring activity of microorganisms exhibit an insignificant decrease in "redness" (axis A in LAB system [22]) of porcelain (A = – 1.55 in sample VB against A = – 1.00 in sample VK), and the color tone values increased.

It is known that increased luminosity in porcelain is caused by a change in its light-diffusing capacity and, consequently, specifics of its macro- and microstructure, which agrees well with the degree of porcelain "ripening" expressed in the coefficient of quartz dissolution and the degree of homogenization of the heterophase matrix (Table 7). The main reason for increased luminosity of porcelain consists in decreased losses in light diffusion related to non-selective absorption. This derives from the fact that the fraction of the vitreous phase in the porcelain increases (from sample ZhO to VS and VB, Table 7) at the expense of the crystalline phase, due mostly to the dissolution of primary mullite and quartz grains, and the secondary needle-shaped mullite is more uniformly distributed over the vitreous phase, considering that agglomerations of primary mullite crystals in the form of druses (clusters) have a negative effect, since these clusters do not participate in light diffusion.

Another reason for the increased luminosity of the porcelain is the reduction of losses due to selective light absorption by the system of color centers, which is confirmed by the decrease in color saturation.

As was earlier mentioned, the chromaticity of porcelain is related to the system and the type of color centers. When mixtures VB and VS with additives of a bacterial culture or a nutrient medium stimulating the growth of natural microflora are maturing, the content of readily soluble, amorphous, and weakly crystallized free ferric compounds increases, and in porcelain firing these compounds form a predominantly paramagnetite phase, whereas part of them are in a magneto-diluted state. Such a state of the iron compounds in firing in a reducing medium facilitates the shift Fe(III) ↔ Fe(II) to the right, which explains the decrease in the "yellow" values in the porcelain (axis B in the LAB system [22]) (from B = 5.83 in sample ZhO to B = 5.49 in sample VS). The decrease in the "red" values in the porcelain can be accounted for in two ways. On the one hand, it can be related to destruction of color centers of the type Fe – O – Fe (iron compounds of the molecular-cluster level forming clusters or associates whose size does not exceed 10 nm; one of the absorption maxima is 565 nm). On the other hand, it can be related to a change in the coordination of polyhedra $[FeO_4]^{3+} \rightarrow [FeO_6]^{3+}$ (for example, one of the absorption maxima (namely, 455 nm) corresponds to Fe in four coordination), which results in de-

creased absorption at the "blue – green" boundary of the reflection spectrum and, accordingly, increased reflection in the blue – green region of the visible spectrum. Both explanations are due to changes in the structure and properties of iron-containing compounds contained in the porcelain mixture in the course of its maturing.

Thus, growth and activity of natural microflora in the maturing of a porcelain mixture occur only on adding a nutrient substrate, which is accompanied by sharp differentiation of microorganisms by layers: aerobic bacteria prevail in the outer layer of the cake, and as for the internal layer, aerobic, facultatively aerobic, and fermenting bacteria actively develop in it at the first stage, and anaerobic bacteria are active at the second stage. Evidently, the change in the color of the internal layer of the cake is related to the transformation of ferric compounds as a result of anaerobiosis.

In the cases where a nutrient medium, or liquid bacterial culture *B. mucilaginosus*, was introduced in porcelain mixtures, similar processes occur in these mixtures on maturing: the optimum molding moisture and the yield point decrease, the strength and apparent density of samples after drying increase, the sintering process is intensified, and the ripening of the porcelain is improved.

The effect of metabolites of *B. mucilaginosus* is manifested even before the cakes are deposited for storage, which is accompanied by disintegration of particles and decreased filterability of the suspension. The increase in the whiteness of the porcelain made of mixtures subjected to maturing is determined, first, by the increase in luminosity related to non-selectivity of light absorption and, second, by the decreased color saturation.

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